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MOCVD OF TlBaCaCuO ON MgO USING FLUORINATED β-DIKETONATE SOURCE REAGENTS

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ABSTRACT

Superconducting $Tl_2Ba_2CaCu_2O_x$ films were fabricated using a three step process. In the first step, amorphous BaCaCuOF films were deposited on MgO(100) single crystal substrates by metalorganic chemical vapor deposition at 500°C using fluorinated β-diketonate complexes of Ba, Ca, and Cu. The fluorine was stripped from the BaCaCuOF films in the second step by annealing in wet O₂ at 785°C. C-axis oriented $Tl_2Ba_2CaCu_2O_x$ films were formed in the final step by annealing the BaCaCuO in dry O₂ at temperatures between 850 and 900°C in the presence of $Tl_2O_3/Ba_2Ca_2Cu_3O_x$ pellets. The physical properties of the films were characterized by SEM, XRD, and RBS, and the electrical properties were evaluated with four point probe and microwave cavity measurements. Resistive transitions as high as 109K have been obtained. The best films showed critical current density as high as 10⁴ A/cm² at 90K and surface resistances 1/2 to 1/5 that of a gold standard at 17 GHz and 77K.

INTRODUCTION

Since the discovery of high temperature superconductors (HTSC), various deposition techniques have been developed to form HTSC thin films. Among the potential applications of HTSCs, passive high frequency devices such as microwave filters and delay lines are considered to be closest to realization. Recent reports of the deposition of TlBaCaCuO with surface resistances of 1 mΩ at 150 GHz (77K) [1] have drawn even more attention to this field. Most microwave and millimeter wave applications will require uniform deposition over large areas. Chemical vapor deposition (CVD) processes, including metalorganic CVD (MOCVD), have been widely used to grow high quality epitaxial films of several semiconductors. However, the difficulty of transporting Ba into the reactor chamber in a controlled and reproducible manner has slowed the development of the MOCVD of HTSC thin films [2], and only few reports have appeared of the MOCVD of TlBaCaCuO films [3,4]. We report the development of a three-step process for the fabrication of superconducting $Tl_2Ba_2CaCu_2O_x$ films in which MOCVD is used to deposit precursor films of BaCaCuOF over large areas, fluorine is removed by an oxygen annealing step, and thallium is in-diffused in a second annealing cycle.

MOCVD OF BaCaCuOF FILMS

The source reagents used in the MOCVD of the precursor films were barium and calcium 1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyloctane-4,6-

dionates ($\text{Ba}(\text{fod})_2$, $\text{Ca}(\text{fod})_2$), and copper hexafluoroacetylacetone ($\text{Cu}(\text{hfacac})_2$). $\text{MgO}(100)$ single crystals were used as substrates and were degreased before loading into the reactor chamber. A double wall reactor chamber was used, and the inner wall temperature was maintained at 200°C to avoid reagent condensation. An inverted vertical reactor configuration was used and the substrates were held facing downward with a pyrolytic boron nitride holder or with mechanical clips made of silver [5]. Two inlet tubes were used to keep the Ba and Ca source reagents separate from the Cu source prior to introduction into the deposition chamber. The deposition was carried out at 4 torr with a susceptor temperature of 500°C.

A key goal of this project has been process reproducibility. The deposition uniformity was evaluated by depositing films over 3 inch silicon wafers and analyzing their compositions by atomic absorption (AA). The films were dissolved in acid solution (HCl or HNO_3). The radial uniformity of the deposition was studied by evaluating the composition of the films at two points in the radial direction. Silicon wafers were cleaved into 1.5 cm X 1.5 cm squares, and squares from the center and perimeter were tested. The cation concentrations at the perimeter normalized to the concentrations in the center are plotted in Figure 1 for five consecutive runs. Ba and Ca variations over 3 inch wafers were found to be within 15%, whereas Cu was always deficient toward the perimeter. As described above, the copper reagent was introduced separately into the reactor chamber through an inlet tube. The carrier gas flow rate in this and the other inlet tubes was found to affect significantly the deposition rate, especially that of Cu, and uniformity. Work is underway to adjust the deposition conditions to improve uniformity.

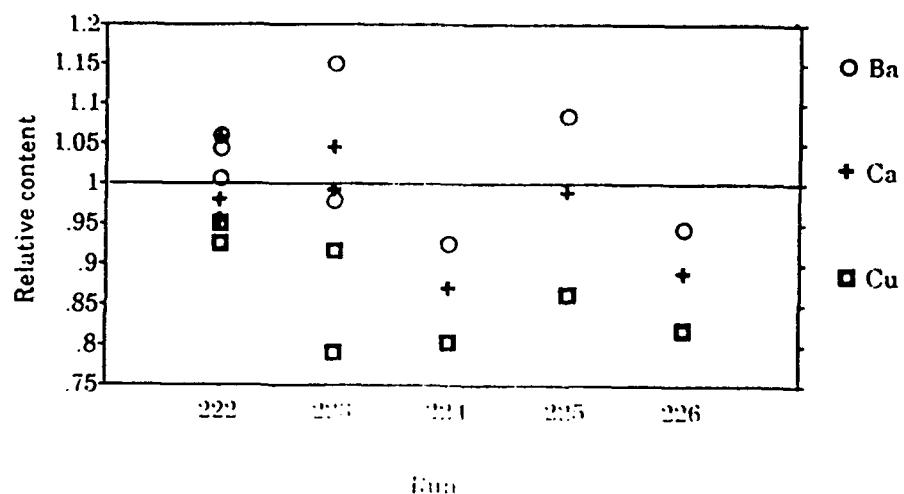


Figure 1. Variation of Ba, Ca, and Cu content in the films. The values are normalized to those at the center of the wafer. Sample 222 and 223 were evaluated at two points near the perimeter.

FLUORINE REMOVAL

The as-deposited films were amorphous mixtures of oxides and fluorides as determined by x-ray diffractometry (XRD) and energy dispersive x-ray (EDX) analysis. This result was consistent with the results of MOCVD experiments in which BaF_2 was formed under similar deposition conditions using $\text{Ba}(\text{fod})_2$ as the sole source reagent [6]. It was found that, although the fluorine was stripped from the BaCaCuOF films during the thallium in-

diffusion step (described below), the desired superconducting phases did not form. Consequently, the fluorine was removed in flowing wet oxygen before proceeding to the thallium in-diffusion step. EDX analysis was used to quantify the efficacy of the fluorine removal during a 60 minute period at temperature. The relative ratio of $K\alpha$ peaks of fluorine to calcium and barium began to fall at temperatures above 550°C (Figure 2).

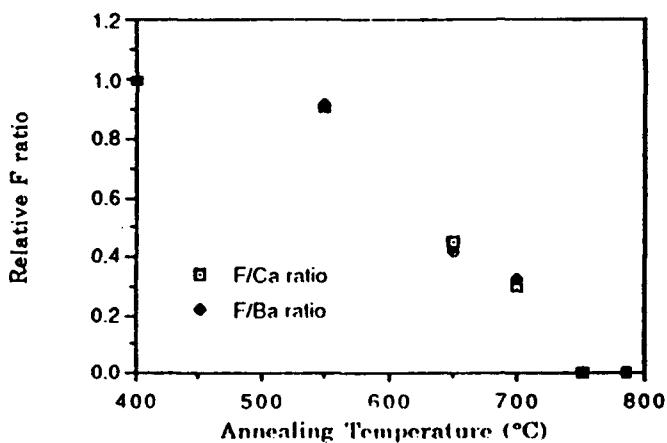


Figure 2. Fluorine content vs annealing temperature. Relative $K\alpha$ peak ratios of F/Ca and F/Ba were normalized to the as-deposited values. Films annealed above 750°C had negligible fluorine peaks.

Fluorine removal was rapid above 750°C. During fluorine removal the film morphology changed from highly porous and uniform to irregular dense grains (Figure 3). When water was omitted from the annealing protocol, large amounts of residual fluorine was present in the films which remained highly porous. A process was developed by which the fluorine removal was monitored during the annealing by bubbling the effluent gas through a water scrubber which trapped the evolved HF. The pH of the water was continually measured and used to calculate total F⁻ evolved. During the first 15 min after the water vapor was introduced into the furnace the pH of the water decreased rapidly, indicating that most of the fluorine was removed during this period. The amount of fluoride trapped in the water estimated from the pH change during the annealing agreed fairly well with that originally in the film as determined by AA, assuming that all Ca and Ba in the as-deposited films was present as the binary fluorides.

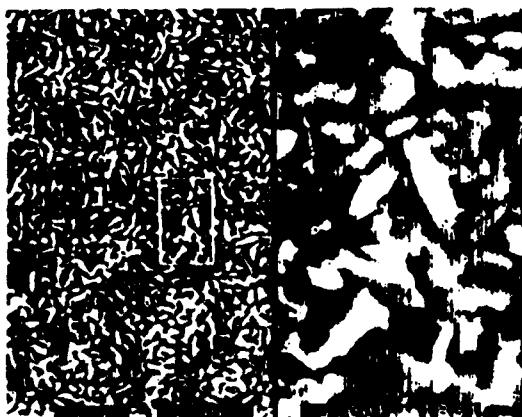


Figure 3. SEM micrograph showing the surface morphology after fluorine removal.

THALLIUM ANNEALING

A second annealing cycle was used to diffuse thallium into the precursor films to form the superconducting phase. The BaCaCuO films were placed between two stoichiometric $Tl_2Ba_2Ca_2Cu_3O$ pellets with the film face down and loaded in a capped alumina boat. The $Tl_2Ba_2Ca_2Cu_3O$ pellets were prepared by mixing appropriate amounts of $BaCuO_2$, Ca_2CuO_3 , and Tl_2O_3 powder to give a $Tl:Ba:Ca:Cu$ molar ratio of 2:2:2:3. After mixing, the powder was pressed into pellets with a pressure of 1.0×10^8 Pa. The fully loaded alumina boat was heated to $870^\circ C$ at approximately $100^\circ C/min$ in an Ar/O_2 atmosphere. The furnace temperature was calibrated by placing a thermocouple at the sample position during a separate calibration run. The sample was kept at the temperature for 10 minutes, the heater power was then shut off and the sample was furnace-cooled to room temperature.

CHARACTERIZATION

The structural properties of the films were evaluated by SEM, XRD, and RBS. Figure 4 (a) shows a SEM of a typical surface morphology where intergrown platelets ranging in size from a few to about five microns are observed. A SEM of a cleaved edge illustrates the surface topology of a fabricated film (Fig. 4 (b)). Some of these smooth plates have dimensions of several tens of microns. XRD was used to identify the phases formed in these films. Figure 5 shows an XRD pattern obtained from the sample whose surface morphology is shown in Fig. 4 (a). The diffraction pattern is dominated by $(00l)$ reflections from $Tl_2Ba_2CaCu_2O_x$ phase. The film shown in Fig. 4 (b) gave a very similar pattern. The x-ray data indicates that the films consist of highly oriented $Tl_2Ba_2CaCu_2O_x$ with the c-axis parallel to the surface normal. Some of the films were characterized by RBS. Analysis of RBS peak intensities gave a reasonable agreement with the XRD data.

The resistivities of the films were measured as a function of temperature using a standard four-point probe method. Silver was sputtered through a mechanical mask and rapidly annealed for 1 min to make electrical contact to the films. Transition temperature, $T_c(R=0)$, of most of the films was in the range between 109K and 100K (See Fig. 6). The best films showed critical current densities as high as 10^4 A/cm² at 90K and surface resistances 1/2 to 1/5 that of a gold standard at 17 GHz and 77K.

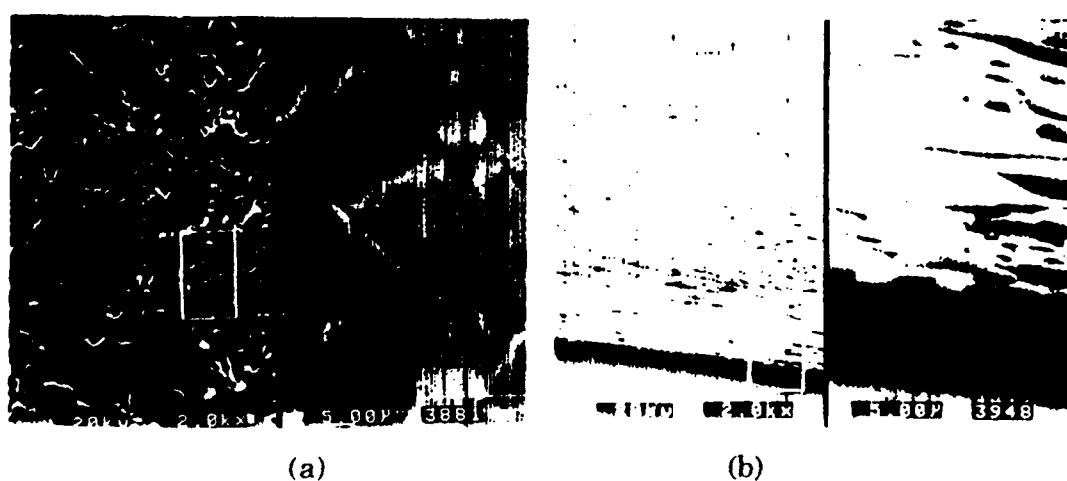


Figure 4. SEM micrographs showing TlBaCaCuO film; (a) surface morphology, (b) cross section.

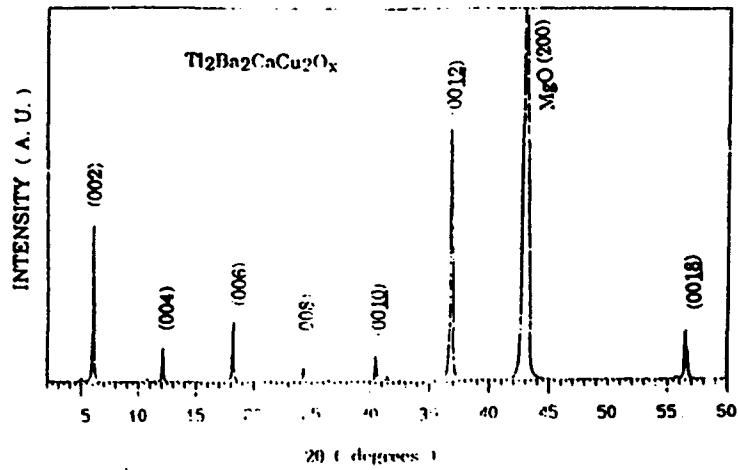


Figure 5. X-ray diffraction curve. The film is highly c-axis oriented $\text{Tl}_2\text{Ba}_2\text{Ca}\text{Cu}_2\text{O}_x$.

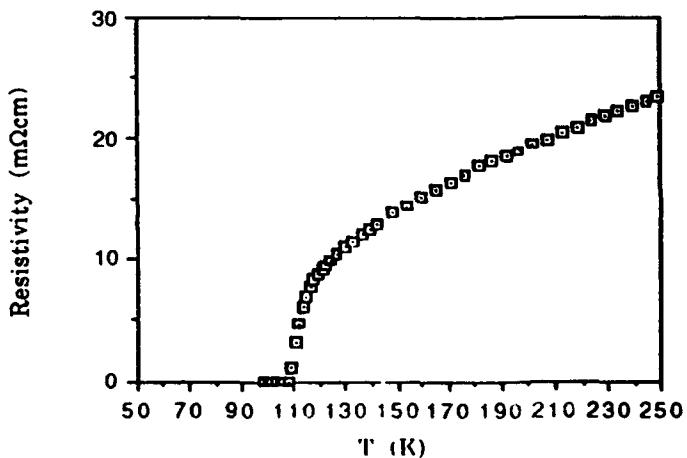


Figure 6. Resistive transition.

SUMMARY

A three-step process consisting of MOCVD and post-annealing was developed to fabricate high quality films. The uniformity of the cation content across 3 inch wafer was evaluated by AA and Ba and Ca were found to be controlled to within 15%. Highly c-axis oriented $\text{Tl}_2\text{Ba}_2\text{Ca}\text{Cu}_2\text{O}_x$ were formed with resistive transitions of 109 K and critical current densities exceeding 10^4 A/cm^2 at 90K.

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